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A Thesis
Submitted to the Department of Metallurgy
in Partial Fulfillment of the
Requirements for the Degree of
Bachelor of Science in Metallurgical Engineering

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Authorities agree that the present volumetric methods for the determination of free cyanide in solutions containing zinc are qualitative rather than quantitative. Moreover, the literature reveals a divergence of opinion as to the form of the double cyanide of zinc with sodium or potassium in aqueous solutions. Analyses of cyanide solutions saturated with $Zn(CN)_2$ show that the molecular ratio of zinc to cyanide is 1 to 4[1] and a salt corresponding to the formula $K_2Zn(CN)_4$ may be readily crystallized from aqueous solutions. L.C. Pan[2] claims to have proven that the sodium zinc complex cyanide in brass plating solutions is $NaZn(CN)_3$.

In preparation and control of brass or zinc plating cyanide baths, it is of great advantage to know what complex cyanides exist in such solutions, in addition to the free cyanide content. Also in the cyanidation of gold ores, a knowledge of the effective cyanide concentration in the circulating solution is highly desirable. Certain mill circuits show a marked tendency to cause the formation of "white precipitate" in the gold precipitation unit. The presence of this substance interferes with the normal precipitation routine and complicates the subsequent refining methods. Knowledge of the nature of cyanide solutions containing zinc is, therefore, of practical as well as academic interest.

(1). Sharwood, W.J., Jour. Am. Chem. Soc. 25 (1903)

(2). Trans. Electrochem. Soc. 62 (1932)

As the method of analysis used up to the present time has failed to give quantitative results in determining the composition of zinc cyanide baths, conductometric methods were adopted in this study. Supplementary tests carried out in this investigation were: volumetric titration with $AgNO_3$ of zinc bearing solutions with KI as an indicator, attempts to dissolve pure $Zn(CN)_2$ in less alkali cyanide than that required to form $K_2Zn(CN)_4$ or $Na_2Zn(CN)_4$, and tests for the solvent action of the double cyanides upon AgCN.

## Theory

The conductance of an aqueous solution of electrolytes depends upon the following factors:

1. The total ionic concentration,
2. The mobilities of the ions present,
3. The temperature of the solution.

Disregarding as constants the ionization of distilled water and the introduction of small quantities of electrolytes from this source, the total ionic concentration is dependent upon the molar concentrations of the electrolytes added and their degrees of dissociation, as only ions carry the electric current. It is essential in conductometric titrations to adjust the concentrations of reagent and sample so that the volume change brought about by the addition of the reagent does not appreciably affect the resistance measurements.

The ions likely to be encountered, in the titration of potassium or sodium zinc complex cyanide solutions with silver nitrate, are listed in Table I with the mobilities of those for which the data were obtainable.

Table I. Mobilities of Ions at 18°C.(3)

| Cations | Mobilities | Anions | Mobilities |
|---|---|---|---|
| $Na^+$ | 43.4 | $NO_3^-$ | 61.8 |
| $K^+$ | 64.4 | $CN^-$ | |
| $Ag^+$ | 54.0 | $Ag(CN)_2^-$ | |
| $\frac{1}{2}Zn^{++}$ | 47 | $\frac{1}{2}Zn(CN)_4^{--}$ | |
| | | $Zn(CN)_3^-$ | |

The fact that the mobilities of the cyanide complexes are low may be correlated with the comparatively high extent of hydration exhibited by complex ions. That ionic migration velocities are affected by their association with molecules of the solvent has been definitely established. Recent investigations tend to show that neither solute ions nor molecules can exist in aqueous solutions without the attachment of one or more molecules of $H_2O$. Moreover, it has been generally observed that for two ions having similar

(3). Taylor, Elementary Physical Chemistry, D. Van Nostrand Co. (1927)

characteristics the lighter exhibits the greater degree of hydration. Accordingly $Zn(CN)_3^-$ should be associated with more water molecules than can be attached to $Zn(CN)_4^{--}$. This assumption, coupled with the fact that the former anion carries only half the charge of the latter, should give rise to a separate branch of the conductometric titration curve if one $CN^-$ radical is removed from the higher complex by $AgNO_3$.

A consideration of the established reactions of $AgNO_3$ with KCN will illustrate their effects upon the conductance of a solution containing no other electrolytes.

$$K^+ + CN^- + AgNO_3 = K^+ + NO_3^- + \underline{AgCN} \qquad (I)$$

$$K^+ + CN^- + \underline{AgCN} = K^+ + Ag(CN)_2^- \qquad (II)$$

$$2K^+ + 2CN^- + AgNO_3 = 2K^+ + NO_3^- + Ag(CN)_2^- \qquad (III)$$

Although the above reactions may not bring about an appreciable change in total ionic concentration, the resulting complex anion should cause a measurable increase in resistance. A deflection in the titration curve should show at the end point of the free cyanide when the following reaction begins,

$$K^+ + Ag(CN)_2^- + AgNO_3 = \underline{2AgCN} + K^+ + NO_3^- \qquad (IV)$$

Additions of silver nitrate subsequent to the complete conversion of the cyanide into AgCN should lower the resistance by increasing the ionic concentration of the solution.

Temperature changes have marked effects on the conductivity of electrolytic solutions. With a rise in temperature the mobility of the ions increases, and the degree of ionization may become greater or less. Care, therefore, should be taken that any one determination is made at constant temperature.

The accuracy and usefulness of the conductance data are primarily dependent upon the following facts:

1. The probability of errors in measurements,
2. The stability of the complex,
3. The purity of the precipitate.

The sensitivity of the electrical measuring instruments and the accuracy of the volumetric devices are important factors to consider in regard to the probability of errors in measurements. Data should be obtained for a sufficient number of points to render occasional errors insignificant. If the speed of the reaction is not sufficiently great to bring about equilibrium within a few minutes following each addition of the reagent, erroneous resistance readings are more likely to be recorded.

The stability of the complex is determined by its ability to remain in the associated state. Bodlander[4] investigated the stabilities of various complexes. The results of his work have later been changed to their reciprocal values in order to show the instability of the complex ions.

(4). Ber. 36, 3399, (1903)

The degree of instability of a complex ion is a measure of its tendency to dissociate according to the general equilibrium reaction.

$$MqAr^{\pm} \rightleftharpoons qM^{+} \quad rA^{-} \qquad (V)$$

From this is derived the mathematical expression for the instability constant,

$$\frac{[M^{+}]^{q} \cdot [A^{-}]^{r}}{[Mq \quad Ar^{\pm}]} = K$$

The instability constants as calculated from the determination of Bodlander for $Ag(CN)_2^{-}$ and $Zn(CN)_4^{--}$ are:

| Complex Ion | Instability Constant |
|---|---|
| $Ag(CN)_2^{-}$ | $1 \times 10^{-21}$ |
| $Zn(CN)_4^{=}$ | $1.3 \times 10^{-17}$ |

This shows that the silver complex is much more stable than the zinc complex. A soluble silver salt should, therefore, decompose the zinc cyanide anion and form the more stable silver complex. For example, if we disregard the probable formation of the intermediate zinc complex anion $Zn(CN)_3^{-}$, the following reaction would be likely to occur,

$$2Ag^{+} + Zn(CN)_4^{--} = 2Ag(CN)_2^{-} + Zn^{++} \qquad (VI)$$

However, if the zinc exists in the form of the anion $Zn(CN)_3^-$ in accordance with the contentions of Pan and others, the probability of its reaction with the silver cation will depend upon the instability constant of $Zn(CN)_3^-$, no estimate of which could be found in the literature. It therefore becomes self-evident that, without consideration of secondary ionization, little light can be thrown on the form of complex zinc cyanide salts in solution by simple volumetric analyses with $AgNO_3$ for a reagent.

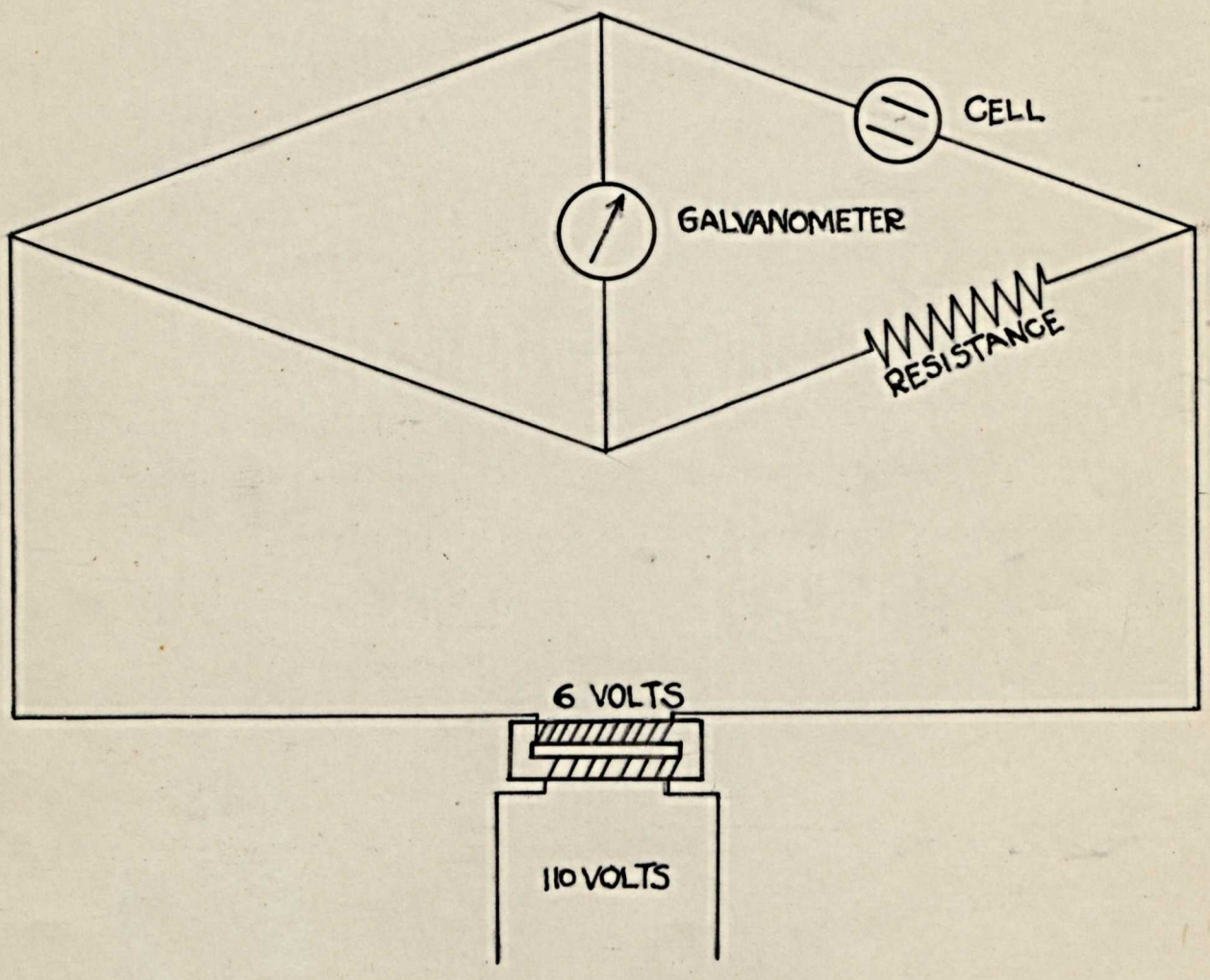
For the linearity desirable in the titration curve a high degree of stability of the complex ion is an obvious requisite.

## Apparatus

The electrical instruments used in this investigation consisted of a Leeds and Northrup direct reading Wheatstone bridge equipped with an A. C. galvanometer and a dipping cell containing platinized electrodes. Figure 1. illustrates diagrammatically the arrangement of the apparatus.

FIGURE NO 1

CONDUCTOMETRIC TITRATION APPARATUS



The use of alternating current is necessary in conductometric titration to prevent concentration changes and cathode deposition as well as to nullify polarization phenomena that would result from electrolysis if direct current were used. The electrodes were frequently replatinized by making each alternately, anode and cathode, in a bath of platinic chloride.

## Preparation of Samples

Zinc cyanide was made by its precipitation with KCN from a concentrated solution of purified $ZnSO_4$. Analysis for zinc in the resulting salt agreed quantitatively with the formula $Zn(CN)_2$. Stock solutions were volumetrically prepared to contain the desired molar concentrations of zinc and total cyanide. The samples pipetted from these solutions were diluted with definite volumes of distilled water before their titration with $AgNO_3$.

## Experimental

The conductometric titrations were conducted at 18°C. Constant agitation of the solution, during the titration and balancing of the bridge was accomplished by continuous stirring with the dipping cell. At the finish of each titration the adhering precipitate was washed from the cell assembly with strong KCN solution and the latter subsequently removed by thorough washing with distilled water. amts + dilution?

As the bridge reading gives the resistance of the cell directly, no attempt was made to calculate conductances. Consequently, resistance readings were plotted against volume, in cubic centimeters, of the reagent. It was found essential to take a large number of readings at small intervals in order to obtain curves that could be interpreted accurately.

## Results

In determining the reactions involved in the titration of zinc bearing cyanide solutions with $AgNO_3$, significant breaks in the conductometric titration curves are of immeasurable assistance.

Curve (1) in Figure 2. illustrates the change in resistance due to the established reactions in the titration of KCN with $AgNO_3$. The formation of the highly associated, slow moving complex, $Ag(CN)_2^-$, according to reaction (III), brings about a marked rise in resistance along line AC. Reaction (IV) evidently controls the change in resistance from C to D, as this part of the titration was characterized by the precipitation of AgCN. The quantity of $AgNO_3$ represented by the horizontal projection of the line AC is equal to the quantity similarly represented by the line CD which is in accordance with reactions I and II. The positions of the two end points give a means of checking the results. Plotting to a larger vertical scale would make the end points appreciably sharper, but the scale used was desirable for comparison with curve (2).

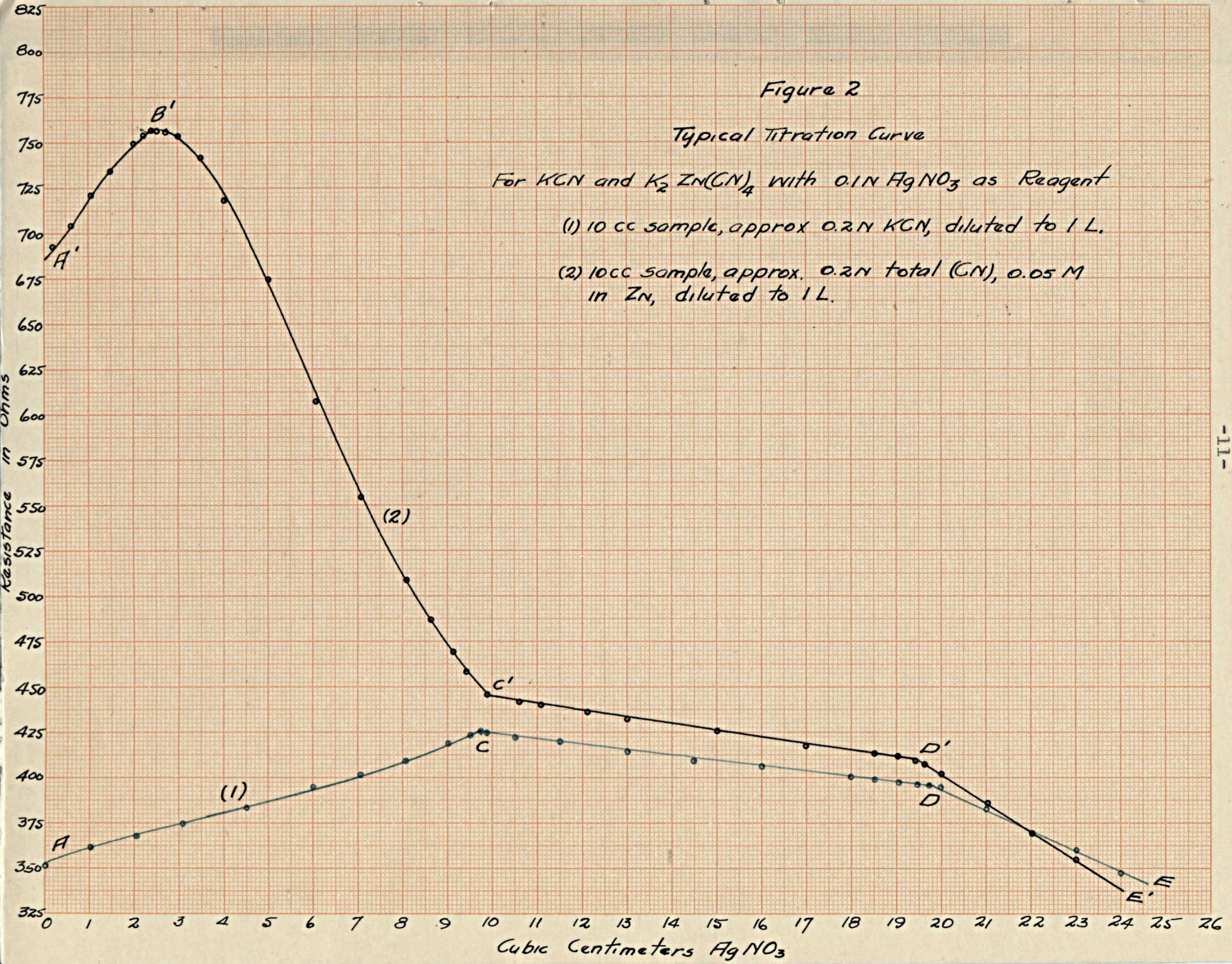


Figure 2
Typical Titration Curve
For KCN and $K_2 Zn(CN)_4$ with 0.1N $AgNO_3$ as Reagent
(1) 10 cc sample, approx 0.2N KCN, diluted to 1 L.
(2) 10cc sample, approx. 0.2N total (CN), 0.05 M in Zn, diluted to 1 L.
Resistance in Ohms
Cubic Centimeters $AgNO_3$
A
A'
B'
C
C'
D
D'
E
E'
(1)
(2)

A consideration of the composition of the sample from which the data for curve (2) was obtained reveals the absence of free cyanide if the formula for the zinc complex is $K_2Zn(CN)_4$. The point C' in this curve marked the initial appearance of the characteristic cloudiness evidenced by the beginning of the formation of AgCN in the titration of pure alkali cyanides. As the samples yielding the two curves were practically identical in total cyanide concentration, point C' marks the end point of the total cyanide in the zinc complex solution. Quite obviously, reaction (IV) establishes the slope of the line C'D'.

It is significant to note that the zinc complex cyanide decomposed completely without the appearance of a precipitate. This is in accord with the theoretical consideration of comparative stabilities of the zinc and silver complex anions. Although the curve from A' to C' shows that Ag and CN have combined in the ratio of 1 to 2, reaction (VI) does not take place directly because there are two branches to that part of the curve which is affected by the decomposition of the compound $K_2Zn(CN)_4$. A consideration of the second branch of the curve will be taken first because the reaction involved is the most obvious. Since the marked drop in resistance from B' to C' demands the liberation $Zn^{++}$, the following reaction will explain this,

$$2KZn(CN)_3 + 3AgNO_3 + KNO_3 \rightarrow 3KAg(CN)_2 + 2Zn(NO_3)_2 \quad \text{(VII)}$$

The presence of silver at C' as the soluble complex has already been established. The branch of the curve involved by the above reaction calls for the molar ratio Zn:Ag::2:3. It is to be observed that this reaction calls for a molecule of $KNO_3$, the presence of which has not been accounted for. That the required $KNO_3$ would be present as a resultant of the previous reaction is not an unreasonable assumption. However, a consideration of the effects of excess cyanide upon the characteristics of the titration curve is essential before the reaction governing the A'B' can be established.

Although the actual free cyanide end points, G and G' in figures 3 and 4 respectively, are not sharp, there is a sufficient upward deflection of the curves at these points to lead to the conclusion that the zinc complex anion originally present undergoes a decomposition by $AgNO_3$ into another less mobile complex. The reaction which suggests itself is, therefore,

$$2\left[Zn(CN)_4^{--} \cdot nH_2O\right] + AgNO_3 \rightarrow 2\left[Zn(CN)_3^{-} \cdot mH_2O\right] + Ag(CN)_2^{-} + NO_3^{-} \qquad \text{(VIII)}$$

in which m is a whole number greater than n.

The titration curves for the zinc complexes shown in figures 2 and 3 were made upon solutions in which the zinc was approximately 0.0005 molar. That reaction (VII) does not strictly hold at higher concentrations is illustrated by figure 4. In this case a precipitate began to form near the

Figure 3

Titration curve for $K_2Zn(CN)_4$ + excess KCN
(Zn in bath 0.0005 M)
10cc sample, approx. 0.05 M Zn, 0.49 N total CN.
Reagent 0.125 N $AgNO_3$.

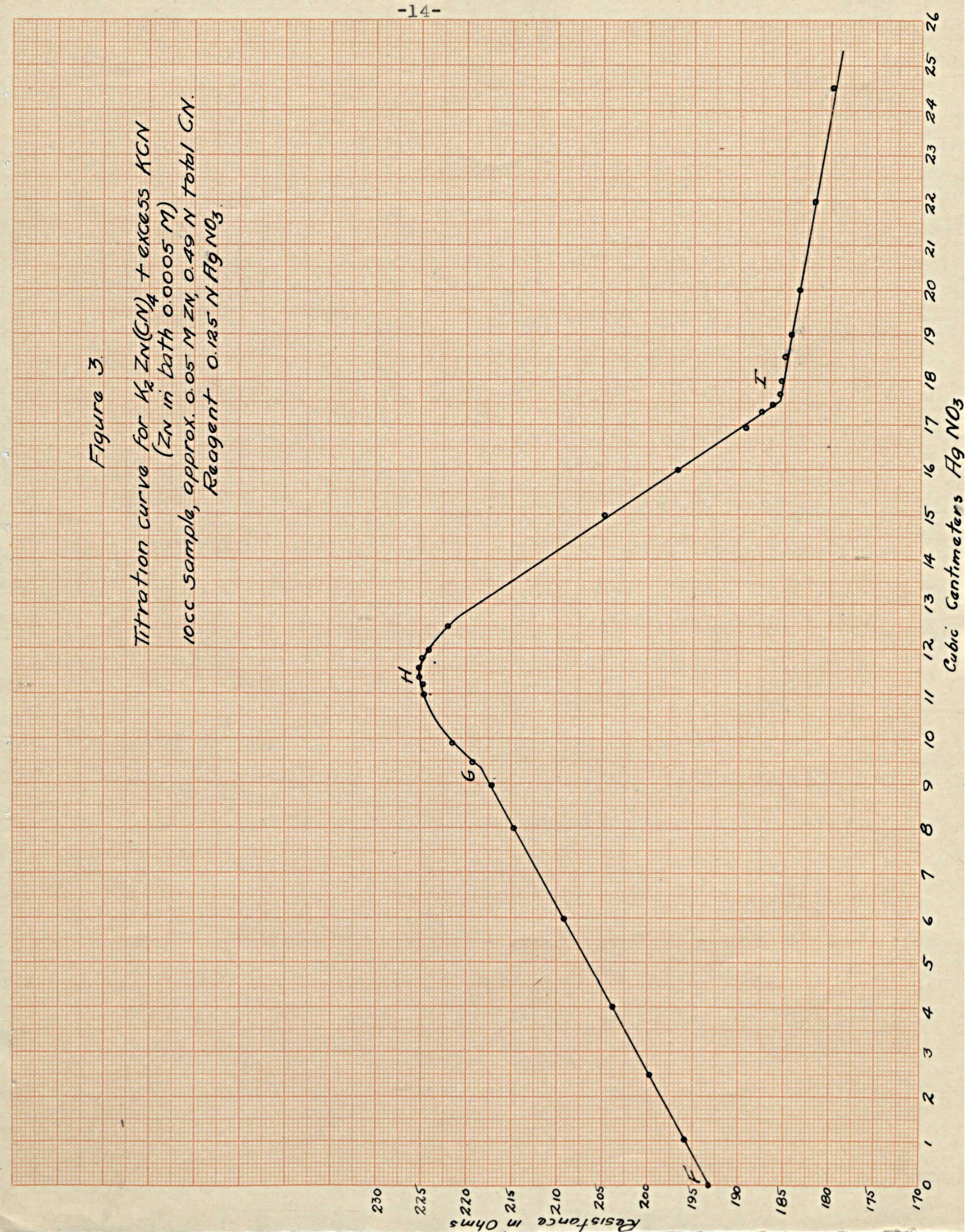
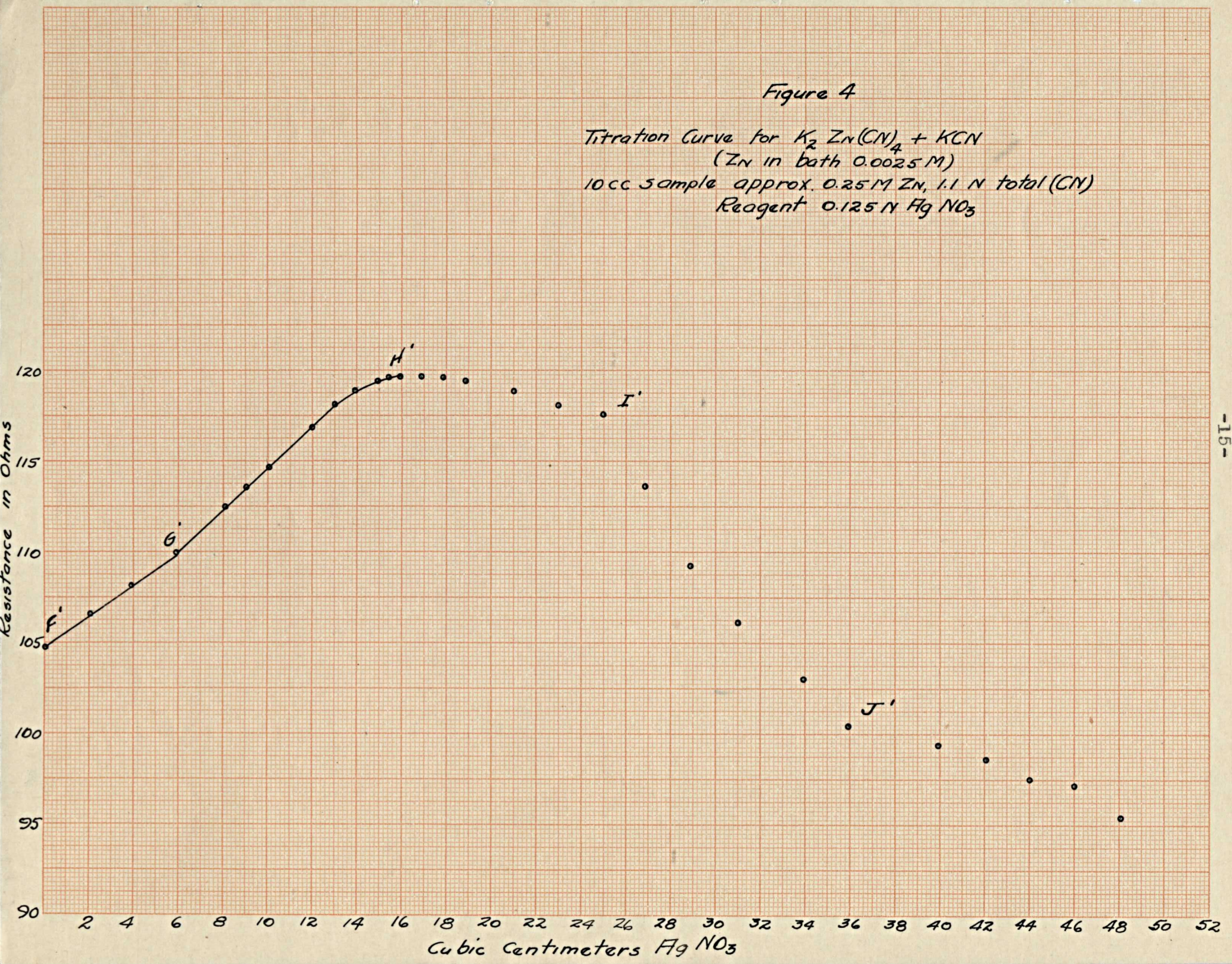


Figure 4

Titration Curve for $K_2 Zn(CN)_4 + KCN$
($Zn$ in bath 0.0025 M)
10 cc sample approx. 0.25 M Zn, 1.1 N total (CN)
Reagent 0.125 N $AgNO_3$



end point of reaction (VIII). However, this precipitate did not possess the appearance of pure AgCN, and the resistance of the cell would not reach stable equilibrium within a reasonable time ($\frac{1}{2}$ hour or more) in its presence. The points to the right of H' show such erratic values that a simple reaction can not be established for the decomposition of $Zn(CN)_3^{--}$ in concentrated solutions. The precipitate may have been a mixture of zinc and silver cyanides precipitating as follows,

$$KZn(CN)_3 + AgNO_3 \rightarrow \underline{AgCN} + \underline{Zn(CN)_2} + KNO_3. \quad (IX)$$

The relatively high concentration of $CN^-$ ions resulting from the secondary ionization of the unstable $KZn(CN)_3$ probably aids in the formation of $Zn(CN)_2$ in preference to the nitrate. That AgCN remains in the precipitate is doubtful because it is soluble in KCN in accordance with reaction (II). That reaction (VII) is also taking place is evidenced by the sharp drop in resistance from I' to J'. The instability of the anion $Zn(CN)_3^-$ is further indicated by the curvature imparted to the titration curves when its concentration becomes significant in the bath. Therefore, a further complication is quite likely introduced by the tendency of $KZn(CN)_3$ to slowly decompose yielding the more stable $K_2Zn(CN)_4$ and liberating $Zn(CN)_2$ as follows,

$$2KZn(CN)_3 \rightleftharpoons K_2Zn(CN)_4 + Zn(CN)_2. \quad (X)$$

The resulting $K_2Zn(CN)_4$ should then react with the AgCN according to the reaction,

$$K_2Zn(CN)_4 + \underline{AgCN} \rightarrow KAg(CN)_2 + KZn(CN)_3 \quad (XI)$$

Reactions (X) and (XI) were substantiated by supplementary laboratory tests. A quarter molar solution of $K_2Zn(CN)_4$ exerted but slight solvent action upon solid AgCN before the precipitation of colloidal $Zn(CN)_2$ took place. The results of the titrations of zinc complex cyanides in the volumetric way were usually slightly higher than the actual free cyanide plus one molecule of cyanide from each molecule of $K_2Zn(CN)_4$ when the titration was made rapidly. In general the longer the time consumed during the titration the lower the volume of $AgNO_3$ required to cause precipitation. The same amount of KI was used in each sample, but in no instance could satisfactory checks be obtained on triplicate samples. The first faint turbidity marking the so called end points bore no resemblance to either AgI or AgCN.

Attempts to dissolve weighed quantities of $Zn(CN)_2$ in less alkali cyanide than that required to form $K_2Zn(CN)_4$ met with no success. The conductometric analyses of the resulting solutions after clarification yielded in all cases the molar ratio of zinc to total cyanide of 1 to 4.

## Conclusions

Although the end points of some of the reactions involved in the titration of zinc bearing cyanide solutions are not sharply defined, the results of conductometric titrations with $AgNO_3$ as reagent are sufficiently quantitative to set forth a few apparent facts.

In the presence of excess alkali cyanide, zinc exists in the anion, $Zn(CN)_4^{--}$.

The volumetric analyses of zinc complex cyanide solutions with $AgNO_3$ in the presence of KI are not even of qualitative value for the detection of the actual free cyanide. Due to the fact that silver forms a more stable complex than does zinc, a soluble silver salt decomposes $Zn(CN)_4^{--}$ giving first the lower complex anion $Zn(CN)_3^{-}$ which is decomposed completely by further additions of the reagent, yielding products depending largely upon the concentration of zinc in the solution.

Little can be said definitely in the light of the increased knowledge brought out by this investigation concerning the cyanidation of gold ores. Sharwood[5] claims some solvent action of the double cyanides of zinc upon gold, especially in the presence of caustic alkali. It is not likely that this solvent action is as great as that of an alkali cyanide solution of one fourth the molar concentration of a solution of $Na_2Zn(CN)_4$ if the time of contact is the same in

(5). Sharwood, W.J., Jour. Am. Chem. Soc. 25 (1903)

each case. The volumetric determination of apparent free cyanide, therefore, does not give a correct measure of the solvent power upon gold and silver of a circulating cyanide solution. Mill practice based on laboratory recoveries with fresh alkali cyanide solutions may not give similar metallurgical results, for the control is based on volumetric titrations of NaCN with $AgNO_3$. Furthermore, it is evident that the so called "white precipitate" will be more likely to form if the base metal cyanides, resulting from the solution of cyanicides and the electrochemical precipitation of gold with metallic zinc, are allowed to build up until the apparent free cyanide is not sufficient to fulfill the solubility requirements of the least stable complex.

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